



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/506,602	09/10/2004	Shahram Miham	257502US0PCT	4911
22850 7590 04/20/2009 OBLON, SPIVAK, MCCLELLAND MAIER & NEUSTADT, P.C. 1940 DUKE STREET ALEXANDRIA, VA 22314				
EXAMINER				
BULLOCK, IN SUK C				
ART UNIT		PAPER NUMBER		
1797				
NOTIFICATION DATE		DELIVERY MODE		
04/20/2009		ELECTRONIC		

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

patentdocket@oblon.com
oblonpat@oblon.com
jgardner@oblon.com

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES

Ex parte SHAHRAM MIHAN
and ZHEIKO MAAS

Appeal 2009-0870
Application 10/506,602
Technology Center 1700

Mailed: April 16, 2009

Before DALE M. SHAW, *Chief Appeals Administrator*.

ORDER RE-MAILING BOARD DECISION

This appeal was originally decided on March 26, 2009 (see attached copy of the decision). The decision, however, inadvertently omitted a copy of the translation noted in footnote (n. 2) on page 2 of the Decision. Accordingly, the Decision is being re-mailed. Appellants' time for seeking rehearing under 37 CFR 41.52(a)(1) expires two (2) months from the entry date of this order.

Appeal 2009-0870
Application 10/506,602

If there are any questions pertaining to this order, please contact the
Board of Patent Appeals and Interferences at 571-272-9797.

Is

OBLON, SPIVAK, MCCLELLAND MAIER & NEUSTADT, P.C.
1940 DUKE STREET
ALEXANDRIA, VA 22314



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/506,602	09/10/2004	Shahram Mihan	257502US0PCT	4911
22850 7590 03/30/2009 OBLON, SPIVAK, MCCLELLAND MAIER & NEUSTADT, P.C. 1940 DUKE STREET ALEXANDRIA, VA 22314				
EXAMINER				
BULLOCK, IN SUK C				
ART UNIT		PAPER NUMBER		
1797				
NOTIFICATION DATE		DELIVERY MODE		
03/30/2009		ELECTRONIC		

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

patentdocket@oblon.com
oblonpat@oblon.com
jgardner@oblon.com

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES

Ex parte SHAHRAM MIHAN
and ZHEIKO MAAS

Appeal 2009-0870
Application 10/506,602
Technology Center 1700

Decided:¹ March 26, 2009

Before EDWARD C. KIMLIN, ADRIENE LEPIANE HANLON, and
MICHAEL P. COLAIANNI, *Administrative Patent Judges*.

HANLON, *Administrative Patent Judge*.

DECISION ON APPEAL

¹ The two-month time period for filing an appeal or commencing a civil action, as recited in 37 C.F.R. § 1.304, begins to run from the Decided Date shown on this page of the decision. The time period does not run from the Mail Date (paper delivery) or Notification Date (electronic delivery).

A. STATEMENT OF THE CASE

This is an appeal under 35 U.S.C. § 134 from an Examiner's decision rejecting claims 1-3 and 5-20 under 35 U.S.C. § 103(a) as unpatentable over Maas.^{2,3} We have jurisdiction under 35 U.S.C. § 6(b). We AFFIRM.

The claims on appeal are directed to a process for the oligomerization of α -olefins wherein the olefin is brought into contact with a specific catalyst system. Claim 1, reproduced below, is the only independent claim on appeal:

1. A process for the oligomerization of α -olefins having at least three carbon atoms, in which the olefin is brought into contact with a catalyst system obtainable from
 - a) at least one chromium source;
 - b) at least one ligand comprising 1,3,5-tri-n-dodecyl-1,3,5-triazacyclohexane; and
 - c) at least one activator comprising a boron compound, with the molar ratio of B:Cr being at least 5.

App. Br., Claims Appendix.⁴

² WO 00/58319 published October 5, 2000. An English translation of this document is of record in the official file of the instant application and is attached hereto. We refer to that translation in this opinion. We note that when referring to WO 00/58319 in the Appeal Brief and Reply Brief, the Appellants cite to portions of US 6,844,290 B1 to Maas. It appears that the disclosure of WO 00/58319 and US 6,844,290 B1 are substantially the same.

³ In the Examiner's Answer, the Examiner withdrew the rejection of claims 1-3 and 5-20 under 35 U.S.C. § 102(b) as anticipated by Maas. Examiner's Answer dated February 7, 2008 ("Ans."), at 2.

⁴ Appeal Brief dated November 13, 2007.

The Appellants argue the patentability of claims 1-3 and 5-20 as a group. *See* App. Br. 7. Thus, we decide the appeal on the basis of independent claim 1. *See* 37 C.F.R. § 41.37(c)(1)(vii) (2007).

B. ISSUES

Issue (1): Have the Appellants shown that the Examiner reversibly erred in concluding that the claimed catalyst system would have been *prima facie* obvious in view of Maas?

Issue (2): On balance, does the evidence of record, including Maas and the Appellants' objective evidence of non-obviousness, weigh in favor of a determination that the subject matter of claim 1 is patentable over Maas?

C. FINDINGS OF FACT

The following findings of fact are supported by a preponderance of the evidence. Additional findings of fact as necessary appear in the Analysis portion of the opinion.

Maas

The invention disclosed in Maas relates to an oligomerization catalyst obtainable from:

- a) a chromium compound CrX_3 and at least an equimolar amount, based on the chromium compound CrX_3 , of a ligand L or an existing chromium complex CrX_3L , in which the groups X are, independently of one another, abstractable counterions and L is a 1,3,5-triazacyclohexane of formula I, and
 - b) at least one activating additive.
- Maas 4:2-10.

The invention also relates to a process for preparing oligomers of olefins using these catalysts. Maas 4:11-12.

Maas discloses that the properties of the catalyst can be influenced by varying the substituents on the 1,3,5-triazacyclohexane ring. Maas 6:17-18.

Maas discloses that the following five (5) 1,3,5-triazacyclohexanes are “especially preferably”:

1,3,5-tri-n-octyl-1,3,5-triazacyclohexane,
1,3,5-tri-n-dodecyl-1,3,5-triazacyclohexane,
1,3,5-tribenzyl-1,3,5-triazacyclohexane,
1,3,5-tris-(2-ethylhexyl)-1,3,5-triazacyclohexane,
1,3,5-tris-(2-n-propylheptyl)-1,3,5-triazacyclohexane.

Maas 8:7-10.

Maas also discloses that the following three (3) activating additives are preferred: (1) an optionally substituted five-member aromatic N-heterocycle and at least one aluminumalkyl, (2) an alkylalumoxane, and (3) at least one boron compound and at least one aluminum alkyl. Maas 12:8-10, 14:15-16, 16:7-9.

Mass discloses several preferred boron compounds. Maas 16:15-17.

According to Maas, the amount of the activating boron compound used is dependent on its nature. The ratio of chromium compound CrX_3 or chromium complex CrX_3L to the activating boron compound is generally from 1:0.1 to 1:10,000, preferably from 1:1 to 1:1,000. Maas 16:18-20.

Maas discloses that the oligomerization catalysts of the present invention make it possible to obtain oligomers of olefins in high yields with a low fraction of by-products. Maas 6:3-5.

D. PRINCIPLES OF LAW

A claimed invention is not patentable if the subject matter of the invention would have been obvious to a person having ordinary skill in the art at the time the invention was made. 35 U.S.C. § 103(a); *KSR Int'l Co. v. Teleflex Inc.*, 127 S. Ct. 1727, 1734 (2007); *Graham v. John Deere Co.*, 383 U.S. 1, 13 (1966).

Facts relevant to a determination of obviousness include (1) the scope and content of the prior art, (2) any differences between the claimed invention and the prior art, (3) the level of skill in the art, and (4) any relevant objective evidence of obviousness or non-obviousness. *KSR*, 127 S. Ct. at 1734; *Graham*, 383 U.S. at 17-18.

Where the difference between the claimed invention and the prior art is some range, the applicant must show that the particular range is critical, generally by showing that the claimed range achieves unexpected results relative to the prior art range. *In re Woodruff*, 919 F.2d 1575, 1578 (Fed. Cir. 1990).

In order for a showing of “unexpected results” to be probative evidence of non-obviousness, it falls upon the applicant to at least establish: (1) that there actually is a difference between the results obtained through the claimed invention and those of the prior art; and (2) that the difference actually obtained would not have been expected by one skilled in the art at the time of invention. *In re Freeman*, 474 F.2d 1318, 1324 (CCPA 1973).

“[O]bjective evidence of nonobviousness must be commensurate in scope with the claims.” *In re Lindner*, 457 F.2d 506, 508 (CCPA 1972).

Furthermore, an applicant relying on comparative tests to rebut a prima facie case of obviousness must compare the claimed invention to the closest prior art. *In re De Blauwe*, 736 F.2d 699, 705 (Fed. Cir. 1984).

If rebuttal evidence of adequate weight is produced, the holding of prima facie obviousness is dissipated and all of the evidence is considered anew. *In re Piasecki*, 745 F.2d 1468, 1472 (Fed. Cir. 1984).

E. ANALYSIS

1. Issue (1)

The Examiner found that Maas expressly teaches the catalytic components recited in claim 1. In particular, the Examiner found that Maas discloses a catalyst obtainable from:

(a) a chromium compound (col. 1, lines 6-8), (b) a 1,3,5-triazacyclohexane ligand (col. 1, lines 12-13), and (c) at least one activating additive (col. 1, line 30). Maas, further, explicitly discloses 1,3,5-tri-n-dodecyl-1,3,5-triazacyclohexane as one of five particularly preferred 1,3,5-triazacyclohexanes (col. 3, lines 12-26; emphasis added by the Examiner). Maas, also, discloses only two combination[s] of activating additives with one of the two being at least one boron compound and at least one aluminum alkyl (col. 7, lines 54-58).

Ans. 4-5.

The Examiner found that Maas discloses a limited number of possible combinations of “particularly preferred” 1,3,5-triazacyclohexanes and activating additives, one of which falls within the scope of claim 1. Ans. 5. The Examiner also found that Maas discloses a molar ratio of boron to chromium that overlaps the claimed range, i.e., “at least 5.” Ans. 4. Thus, the Examiner concluded that the claimed catalyst would have been prima facie obvious in view of Maas.

The Appellants recognize:

Maas does, in fact, disclose that catalysts can separately include chromium compounds CrX_3 (*see* column 4, line 51 to column 5, line 4), 1,3,5-tri-*n*-dodecyl-1,3,5-triazacyclohexane (*see* column 3, lines 22 to 23), and a boron compound (*see* column 7, line 54 to column 8, line 4).

App. Br. 4.

Nonetheless, the Appellants argue that the Examiner has failed to demonstrate why one of ordinary skill in the art would have been motivated to select the particular combination of components recited in claim 1 from the numerous chromium compounds, 1,3,5-triazacyclohexanes, and activating additives disclosed in *Maas*. App. Br. 4; Reply Br. 2.⁵ In addition, the Appellants argue that *Maas* would not have guided one of ordinary skill in the art to select a B:Cr molar ratio within the range recited in claim 1. Reply Br. 2.

The Appellants' arguments are not persuasive of reversible error. *Maas* discloses a catalyst obtainable from a chromium source, a 1,3,5-triazacyclohexane, and at least one activating additive. *Maas* 4:2-10. We recognize that *Maas* discloses a number of 1,3,5-triazacyclohexane compounds and activating additives. *See, e.g.*, *Maas* 7:1-10, 12:8-16:17. However, *Maas* also discloses a limited class of catalysts obtainable from one of five (5) especially preferred 1,3,5-triazacyclohexanes and one of three (3) preferred classes of activating additives. *Maas* 8:7-10; 16:7-9. This limited class consists of fifteen (15) catalysts.

We find that one of ordinary skill in the art would have immediately envisaged each catalyst of this limited class, which includes a catalyst within

⁵ Reply Brief dated April 7, 2008.

the scope of claim 1 (i.e., a catalyst obtainable from a chromium source, a 1,3,5-tri-n-dodecyl-1,3,5-triazacyclohexane, and an activator comprising a boron compound). *See In re Schaumann*, 572 F.2d 312, 316-17 (CCPA 1978) (disclosure, embracing very limited number of compounds, provides a description of those compounds just as surely as if they were identified by name); *In re Petering*, 301 F.2d 676, 681 (CCPA 1962) (disclosure describes not only a broad class but also a much more limited class within the broad class; one skilled in the art would, on reading the disclosure, at once envisage each member of this limited class).

As for the recited “molar ratio of B:Cr being at least 5,” the Appellants have not pointed to any error in the Examiner’s finding that Maas discloses a molar ratio of B:Cr that overlaps this range. Thus, the Appellants must show that the claimed range is critical. *Woodruff*, 919 F.2d at 1578.

In sum, the Appellants have not shown that the Examiner reversibly erred in concluding that the claimed catalyst system would have been *prima facie* obvious in view of Maas.

2. Issue (2)

In an attempt to rebut the *prima facie* case of obviousness, the Appellants argue that Examples in the Appellants’ Specification demonstrate that catalysts according to the present invention provide superior results relative to the catalysts of Maas. In particular, the Appellants compare the results of Examples 1 and 2 with the results of Comparative Examples 3 and 4 reported in the Table on page 6 of the Specification and argue that the claimed catalysts provide “superior results.” App. Br. 5-6.

The Table is reproduced below:

Table

Ex.	Cat { μmol }	DMAB*	TIBAL**	DEAC**	Activity kgC ₁₂ /mol _{Cr} /h
1	39.4	10	50	5	283
2	38.5	10	50	~	175
3***	40.6	2	50	~	130
4***	38.1	10	50	~	67

* Molar ratio of B:Cr

** Molar ratio of Al:Cr

*** Comparative examples

Spec. 6.

According to the Specification, 1-Butene was oligomerized using each of the catalyst systems in Examples 1 and 2 and Comparative Examples 3 and 4. Spec. 6:7-8.

Examples 1 and 2 and Comparative Example 3 used [(1,3,5-tri-n-dodecyl-1,3,5-triazacyclohexane)CrCl₃], and Comparative Example 4 used [(1,3,5-tris(2-ethylhexyl)-1,3,5-triazacyclohexane)CrCl₃]. Spec. 5:42-45. According to the Appellants, Comparative Example 4 corresponds to Maas Example 21. Spec. 5:45; App. Br. 5.

The same boron compound was used in each of the examples, i.e., dimethylanilinium tetrakis(pentafluorophenyl)borate (DMAB). Spec. 6:1-3.

We make the following observations regarding the results reported in the Table:

1. The Appellants have failed to direct us to any evidence establishing that the activity reported in the Table would have been unexpected. *Freeman*, 474 F.2d at 1324.
2. The Appellants have failed to demonstrate that the evidence is commensurate in scope with the claims. In particular, claim 1 recites a process for the oligomerization of a number of α -olefins, i.e., α -olefins having at least three carbon atoms. See Spec. 5:10-15. However, the Table only reports the results of oligomerizing a single α -olefin (1-butene).

Likewise, the claimed catalyst system encompasses a wide range of chromium sources and boron compounds as well as a broad molar ratio of B:Cr, i.e. “at least 5.” See, e.g., Spec. 3:5-13, 4:4-13. However, the examples said to embody the claimed invention (Examples 1 and 2) only use a catalyst system obtained from a single chromium source (CrCl_3) and a single boron compound (DMAB) with one B:Cr molar ratio (10).

The Appellants argue that “the nonobviousness of a genus can be supported by data showing unexpected results for a species.” The Appellants cite *In re Kollman*, 595 F.2d 48 (CCPA 1979) for support. Reply Br. 4.

In *Kollman*, the Court explained:

We feel that the obviousness of a broader claimed range can, in certain instances, be proven by a narrower range of data. Often, one having ordinary skill in the art may be able to ascertain a trend in the exemplified data which would allow him to reasonably extend the probative value thereof. The proof, thus considered, might then be sufficient to rebut a PTO holding of prima facie obviousness.

Kollman, 595 F.2d at 58.

In this case, the Appellants have failed to demonstrate that one of ordinary skill in the art would be able to ascertain a trend in the results reported in Examples 1 and 2.

3. The Appellants have failed to establish that Comparative Example 4 (i.e., Maas Example 21) is the closest prior art. *De Blauwe*, 736 F.2d at 705.

The Examiner maintains that Maas Example 4 (i.e., “Chromium complex 3”: $[(1,3,5\text{-tri-}n\text{-dodecyl-1,3,5-triazacyclohexane})\text{CrCl}_3]$) is the

closest prior art because this catalyst “is the same catalyst as recited in claim 1.” Ans. 6.

On the other hand, the Appellants argue that Comparative Example 4 (i.e., Maas Example 21) is the closest prior art because this example satisfies more claim limitations (i.e., boron compound, B:Cr molar ratio) than Maas Example 4 (i.e., ligand). The Appellants rely on *In re Merchant*, 575 F.2d 865, 868 (CCPA 1978) for support. Reply Br. 3.

In *Merchant*, the Court explained:

Given the enormous variety of technologies and claimed subject matter, no all-encompassing principle or test can be delineated for determining the closest prior art. However, an almost self-evident guideline would appear effective in most cases. A comparison of the claimed invention with the disclosure of each cited reference to determine the number of claim limitations in common with each reference, bearing in mind the relative importance of particular limitations, will usually yield the closest single prior art reference.

Merchant, 575 F.2d at 868.

In this case, the Appellants have failed to direct us to any evidence establishing that the particular boron compound and B:Cr molar ratio selected is more important in the claimed process than the particular ligand chosen.

On balance, the evidence of record, including Maas and the Appellants’ objective evidence of non-obviousness, does not weigh in favor of a determination that the subject matter of claim 1 is patentable over Maas.

F. DECISION

The decision of the Examiner is affirmed.

Appeal 2009-0870
Application 10/506,602

No time period for taking any subsequent action in connection with this appeal may be extended under 37 C.F.R. § 1.136(a). *See* 37 C.F.R. § 1.136(a) (2008).

AFFIRMED

ssl

OBLON, SPIVAK, MCCLELLAND MAIER & NEUSTADT, P.C.
1940 DUKE STREET
ALEXANDRIA VA 22314

PTO 09-3594

CC = WO
20001005
A1
0058319

OLIGOMERIZATION CATALYST
[Oligomerisierungskatalysator]

Heiko Maas et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. MARCH 2009
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	WO
DOCUMENT NUMBER	(11):	0058319
DOCUMENT KIND	(12):	A1
PUBLICATION DATE	(43):	20001005
APPLICATION NUMBER	(21):	PCT/EP00/02660
APPLICATION DATE	(22):	20000325
INTERNATIONAL CLASSIFICATION ⁷	(51):	C 07 F 11/00
		C 07 C 29/16
		2/32
		B 01 J 31/18
PRIORITY COUNTRY	(30):	US
PRIORITY NUMBER	(30):	09/277,823
PRIORITY DATE	(30):	19990329
PRIORITY COUNTRY	(30):	DE
PRIORITY NUMBER	(30):	19922048.4
PRIORITY DATE	(30):	19990514
PRIORITY COUNTRY	(30):	DE
PRIORITY NUMBER	(30):	19943544.8
PRIORITY DATE	(30):	19990911
INVENTORS	(72), (75):	Heiko Maas et al.
APPLICANT(S)	(71):	BASF Aktiengesellschaft
DESIGNATED CONTRACTING STATES		
(national):	(81):	CN, JP, KR, SG, US, European Patent (AT, BE,

CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT,

LU, MC, NL, PT, SE)

TITLE

(54): OLIGOMERIZATION CATALYST

FOREIGN TITLE

[54A]: Oligomerisierungskatalysator

FOR INFORMATION ONLY

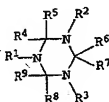
Codes for the identification of PCT contract states on the cover sheets of the documents that publish the international applications in accordance with the PCT

AL	Albania	IE	Ireland	PT	Portugal
AM	Armenia	IL	Israel	RO	Romania
AT	Austria	IS	Iceland	RU	Russian Federation
AU	Australia	IT	Italy	SD	Sudan
AZ	Azerbaijan	JP	Japan	SE	Sweden
BA	Bosnia-Herzegovina	KE	Kenya	SG	Singapore
BB	Barbados	KG	Kyrgyzstan	SI	Slovenia
BE	Belgium	KP	Democratic People's Republic of Korea	SK	Slovakia
BF	Burkina Faso	KR	Republic of Korea	SN	Senegal
BG	Bulgaria	KZ	Kazakhstan	SZ	Swaziland
BJ	Benin	LC	Saint Lucia	TD	Chad
BR	Brazil	LI	Liechtenstein	TG	Togo
BY	Belarus	LK	Sri Lanka	TJ	Tajikistan
CA	Canada	LR	Liberia	TM	Turkmenistan
CF	Central African Republic	LS	Lesotho	TR	Turkey
CG	Congo	LT	Lithuania	TT	Trinidad and Tobago
CH	Switzerland	LU	Luxembourg	UA	Ukraine
CI	Côte d'Ivoire	LV	Latvia	UG	Uganda
CM	Cameroon	MC	Monaco	US	United States of America
CN	China	MD	Republic of Moldavia	UZ	Uzbekistan
CU	Cuba	MG	Madagascar	VN	Vietnam
CZ	Czech Republic	MK	Macedonia (former Yugoslavian Republic of Macedonia)	YU	Yugoslavia
DE	Germany			ZW	Zimbabwe
DK	Denmark	ML	Mali		
EE	Estonia	MN	Mongolia		
ES	Spain	MR	Mauritania		
FI	Finland	MW	Malawi		
FR	France	MX	Mexico		
GA	Gabon	NE	Niger		
GB	United Kingdom	NL	Netherlands		
GE	Georgia	NO	Norway		
GH	Ghana	NZ	New Zealand		
GN	Guinea	PL	Poland		
GR	Greece				
HU	Hungary				

Description

This invention concerns an oligomerization catalyst for olefins that can be obtained from

a) a chromium compound CrX_3 and an at least equimolar amount, with respect to the chromium compound CrX_3 , of a ligand L, or a prepared chromium complex CrX_3L , in which the groups X independently stand for abstractable counterions and L stands for a 1,3,5-triazacyclohexane of formula I



in which the groups $\text{R}^1\text{-R}^9$ independently have the following meanings: hydrogen or Si-organic or optionally substituted C-organic groups with 1-30 C atoms, where two geminal or vicinal residues $\text{R}^1\text{-R}^9$ can also be bonded to a five- or six-member ring, and

b) at least one activating additive.

In addition, this invention concerns a method for producing oligomers of olefins using the new catalysts, the resulting oligomers, and the oxo alcohols obtainable from these oligomers.

Olefin oligomers with up to 30 carbon atoms have great economic importance as copolymers for plastics (for example, 1-hexene) or as precursors for oxo alcohols (for example, 1-hexene and the decenes and tetradecenes), while the latter are in turn components of surfactants and plasticizers for plastics. In the product associations of the chemical industry therefore the oligomerization processes are a central step from the industrial olefin streams that derive from steam cracking, for instance, to the products of everyday use.

The use of catalysts that contain compounds of chromium, amines and aluminum compounds in the oligomerization of α -olefins is generally known:

According to EP-A 780 353 olefins can be oligomerized, in particular trimerized, in the presence of a chromium source, a pyrrole-containing compound and a metal alkyl. However, the preparation of the catalyst involves a loss of active components.

An oligomerization catalyst for α -olefin that, besides a chromium compound and an aluminum compound, additionally contains at least one nitrogen-containing compound, which can be a pyrrole, is known from DE-A 196 07 888. Here, too, preparation of the catalyst involves high losses, in correspondence with EP-A 780 353.

EP-A 537 609 teaches a process in which ethylene is converted to a mixture of α -olefins with a higher fraction of 1-hexene in the presence of a chromium complex with a coordinating polydentate ligand and an aluminoxane. However, because of the low catalyst activity and at the same time, low trimer selectivity, the economy of the described process is unsatisfactory.

Experiments on selective trimerization of ethylene to form 1-hexene with an N,N,N-trioctyl-triazacyclohexane-chromium complex and methylalumoxane was reported at the 215th ACS National Meeting, March 29 - April 2, 1998, in Dallas, Texas. However, the catalyst is only moderately active and it still leads to considerable amounts of polymer products, which is disadvantageous for the economy of the process.

This invention, therefore, was based on the task of finding more cheaply obtainable and stable catalysts with improved activity and selectivity for lower-molecular oligomers of olefins.

Accordingly, the oligomerization catalyst noted at the start was found.

* [Numbers in right margin indicate pagination of the original text.]

Moreover, a method for producing oligomers of olefins using the new catalysts, the oligomers obtained in this way, and the oxo alcohols obtained from these oligomers were found.

Oligomers of olefins can be obtained with high yields and with a low fraction of byproducts, whose molecular weight M_w is greater than 500, can be obtained with the oligomerization catalysts in accordance with the invention. In particular, the catalyst is characterized by high selectivity with regard to the trimerization of α -olefins and above all, ethene. /3

Triazacyclohexane and its derivatives, which differ by different substitution patterns at the ring atoms, have been known for a long time and have diverse uses in industry, since for the most part they can be produced from readily available starting materials in a simple and cheap way. For instance, triazacyclohexane derivatives are used in the desulfurization of kerosene. The use of triazacyclohexane and its derivatives as ligands in the production of organometal complexes, however, is not very common. There are only isolated instances of descriptions of complexes with these ligands in the organometal literature, for example: J. Chem. Soc., Dalton Trans. (1997), 1363-1368; Z. Naturforsch., Part B50 (1995), 1038-1043; Angew. Chem. Int. Ed. Engl. 33 (1994), 1877-1878; J. Organomet. Chem. 501 (1995), 303-307; Chem. Ber. 129 (1996), 25-27; J. Organomet. Chem. 520 (1996), 121-129; Inorg. Chem. 36 (1997), 6064-6069; Chem. Ber. 129 (1996), 1327-1333.

The properties of the catalyst in accordance with the invention can be affected by varying the substituents on the 1,3,5-triazacyclohexane ring. Thus, the catalyst activity can normally be increased by substituents, especially on the nitrogen atom. In addition, through the choice and geometry of the substituents the accessibility of the central atom for the α -olefins that are to be converted can be controlled and with that, the selectivity of conversion with regard to various starting olefins as well. The chemical structure of the substituents R^1 - R^9 , therefore, can be varied in wide ranges in order to obtain a catalyst tailored to the relevant conversion.

Possibilities as optionally substituted C organic groups on the 1,3,5-triazacyclohexane ring are, for example:

- C₁-C₁₈ alkyl, preferably C₁-C₁₂ alkyl such as methyl, ethyl, N,N-dimethylaminoethyl, n-propyl, isopropyl, butyl, pentyl, hexyl, 2-ethylhexyl, heptyl, octyl, nonyl, decyl, dodecyl, 1,1-dimethyldodecyl,
- 5- to 7-member cycloalkyl, which in turn can have a C₁-C₁₀ aryl group as substituent, such as cyclopentyl and cyclohexyl,
- C₆-C₁₅ aryl such as phenyl, o-tolyl, p-tolyl, m-tolyl, 1-naphthyl and 2-naphthyl, or
- C₆-C₁₅ arylalkyl, preferably C₆-C₈ arylalkyl such as benzyl and (1-phenyl)ethyl.

/4

Possibilities as Si-organic groups are, for example: trialkylsilyl groups with 1-10 C atoms in like or different alkyl residues, especially trimethylsilyl groups.

Substituents in the C-organic groups or Si-organic groups on the 1,3,5-triazacyclohexane ring can in particular, be alkyl groups with donor groups. The donor group can be neutral or anionic and can contain a heteroatom of groups 15-16 of the periodic system (IUPAC proposal 1985) or can be a carbanion. If it is neutral, then it can be coordinatively bonded to the chromium. Preferably it is coordinated to the chromium. If the donor is formally anionic, it is covalently bonded to the metal center. The bonds can be intra- or intermolecular, preferably intramolecular. Neutral donors with oxygen and/or nitrogen atoms that have free electron pairs, where the oxygen and/or nitrogen atoms can also be inserted into an alkyl chain, are preferred.

1,3,5-Triazacyclohexane ligands in which the groups R¹, R² and R³ independently stand for optionally substituted C₁-C₁₂ alkyl, C₆-C₁₅ aryl or C₆-C₈ arylalkyl, especially optionally substituted C₁-C₁₂ alkyl or C₆-C₈ arylalkyl like methyl, ethyl, N,N-dimethylaminoethyl, n-propyl, n-butyl, tert-butyl, hexyl, octyl, dodecyl, 1,1-dimethyldodecyl, (1-phenyl)ethyl, are preferred.

1,3,5-Triazacyclohexane ligands in which the groups R^4 , R^5 , R^6 , R^7 , R^8 and R^9 independently stand for hydrogen or C_1 - C_4 alkyl and especially hydrogen or methyl are preferably used in the process in accordance with the invention.

Preferred 1,3,5-triazacyclohexanes are 1,3,5-tri-tert-butyl-1,3,5-triazacyclohexane, 1,3,5-triethyl-1,3,5-triazacyclohexane, 1,3,5-tris-[(1-phenyl)ethyl]-1,3,5-triazacyclohexane, 1,3,5-tris-[(1,1-dimethyl)dodecyl]-1,3,5-triazacyclohexane and 1,3-di-n-dodecyl-5-[2-(N,N-dimethylamino)ethyl]-1,3,5-triazacyclohexane and especially preferably 1,3,5-tri-n-octyl-1,3,5-triazacyclohexane, 1,3,5-tri-n-dodecyl-1,3,5-triazacyclohexane, 1,3,5-tribenzyl-1,3,5-triazacyclohexane, 1,3,5-tris-(2-ethylhexyl)-1,3,5-triazacyclohexane, 1,3,5-tris-(2-n-propylheptyl)-1,3,5-triazacyclohexane.

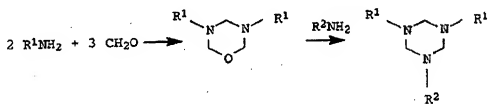
The 1,3,5-triazacyclohexanes of general formula I in which the groups R^4 - R^9 stand for hydrogen and the groups R^1 - R^3 are the same can be prepared in a substantially known way, for example by the reaction of primary amines of the type R^1NH_2 with formaldehyde or paraformaldehyde. The 1,3,5-triazacyclohexanes that have one each methyl group and hydrogen atom on the carbon atom of the ring are correspondingly accessible via acetaldehyde. /5

Also, the 1,3,5-triazacyclohexanes of general formula I in which at least one of the residues R^1 , R^2 or R^3 is different from the other two of these residues can be produced in a substantially known way (for example, see Beilstein, "Handbook of Organic Chemistry," 4th Ed., Vth Suppl. Series, Springer-Verlag, Berlin, Vol. 26 (1986) pp. 3 ff. and literature cited there; R = octyl: J. Polym. Sci., Polym. Chem. Ed. 329 (1993), 1941-1958; J. Prakt. Chem. 727 (1985), 739-748; EP-A 620 266; DE-A 24 31 862; DE-A 41 00 856; Pharmazie 30 (1975), 699-706). As examples, some of the known production methods are briefly outlined here:

1) The reaction of a mixture of two primary amines (R^1NH_2 and R^2NH_2) with formaldehyde (as aqueous solution or paraformaldehyde) leads to a mixture of various products, which can be separated as follows:

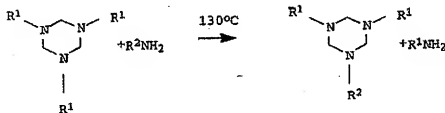
- Distillation with sufficiently small R^1 and R^2 .
- Carrying out of the reaction with a large excess of the amine R^1NH_2 if the symmetric reaction product can be distilled out. After distillation there then remains the unsymmetric product.
- Selective crystallization of a product.
- Complexing the mixture of the 1,3,5-triazacyclohexanes with the chromium compound, for instance $CrCl_3$, and separation of the resulting chromium complexes, for instance by column chromatography.

2) Reaction of an amine R^1NH_2 with an excess of formaldehyde to form a mixture of symmetrically substituted 1,3,5-triazacyclohexane and the corresponding 1-oxa-3,5-diazacyclohexane; in a second step the 1-oxa-3,5-diazacyclohexane is reacted with an amine R^2NH_2 (optionally with acid catalysis), where the ring oxygen is exchanged for an R^2N group.



The separation of the product mixture can take place as under (1).

3) Reaction of a symmetric 1,3,5-triazacyclohexane with small R^1 (methyl or ethyl) at about 130°C with an amine $R^2\text{NH}_2$. At this temperature $R^1\text{NH}_2$ escapes and a mixture of the unsymmetric 1,3,5-triazacyclohexanes is formed.



The separation can take place as under (1).

4) Reaction of two different symmetric 1,3,5-triazacyclohexanes with each other, with exchange of substituents taking place. The products can be separated as under (1).

Any of the abstractable counterions that are suitable for this purpose in organometal chemistry are suitable as group X in the chromium compounds CrX_3 or the chromium complexes CrX_3L , in particular

- halogens like fluorine, bromine, iodine and above all, chlorine,
- tosylate, triflate, tetrafluoroborate, hexafluorophosphate, hexafluoroantimonate, tetraphenylborate,
- $\text{C}_1\text{-C}_{10}$ carboxy, and above all, 2-ethylhexanoate,
- alkyl groups, especially methyl, ethyl, isopropyl, phenyl, benzyl,
- bulky non-coordinating anions like $\text{B}(\text{C}_6\text{F}_5)_4^-$.

The groups X are chosen in particular so that the chromium compounds CrX_3 or chromium complexes CrX_3L that contain them have good solubility in the solvent that is used in each case.

As starting substances for the chromium compounds CrX_3 and the chromium complexes CrX_3L one uses, for instance, chromium halides like CrCl_3 , CrBr_3 , $\text{Cr}(\text{triflate})_3$, $\text{Cr}(\text{III})$ alkoxylates like 2-ethyl

hexanoate and complexes of these chromium compounds with weakly bonded neutral complex ligands, which can be displaced by the 1,3,5-triazacyclohexane and optionally by the 5-member aromatic N-heterocycle, for example, ether complexes like CrCl_3 (tetrahydrofuran)₃, CrCl_3 (dioxane)₃, ester complexes like CrCl_3 (n-butyl acetate), CrCl_3 (ethyl acetate), alcohol complexes like CrCl_3 (isopropanol)₃, CrCl_3 (2-ethylhexanol)₃, amine complexes like CrCl_3 (pyridine)₃, CrCl_3 (isopropylamine)₂, or nitrile complexes like CrCl_3 (acetonitrile)₃ acetonitrile.

In a preferred embodiment of the process in accordance with the invention oligomerization catalysts that were prepared using chromium complexes CrX_3L that were especially prepared and isolated beforehand are used.

The chromium complexes CrX_3L can be obtained in general by methods known to one skilled in the art or methods analogous to such methods (for instance, see W. A. Herrmann, A. Salzer: "Synthetic Methods of Organometallic and Inorganic Chemistry," Vol. 1 - Literature, Laboratory Techniques, and Common Starting Materials, Thieme Publishers, Stuttgart, 1996).

If the chromium complexes CrX_3L are prepared in situ, as a rule, the chromium compound CrX_3 is dissolved or suspended in the reaction medium and the 1,3,5-triazacyclohexane is added as desired in bulk or in dissolved form.

In the oligomerization process in accordance with the invention the use of chromium complexes CrX_3L , in which X and L have the following meanings, is preferred:

X independently means halogen, tosylate, triflate, alkyl

L means 1,3,5-triazacyclohexanes of formula I, in which the groups R^4 , R^5 , R^6 , R^7 , R^8 and R^9 independently stand for hydrogen or C₁-C₄ alkyl and especially hydrogen or methyl and in which R^1 , R^2 and R^3 independently stand for methyl, ethyl, N,N-dimethylaminoethyl, propyl, n-butyl, tert-butyl, hexyl, octyl, dodecyl, 1,1-dimethyldodecyl or (1-phenyl)ethyl.

Especially preferred is the use of chromium complexes CrX_3L in which X and L have the following meanings:

X independently means chlorine, tosylate

L means 1,3,5-triazacyclohexanes of formula I in which the groups $\text{R}^4, \text{R}^5, \text{R}^6, \text{R}^7, \text{R}^8$ and R^9 independently stand for hydrogen or methyl and in which R^1, R^2 and R^3 independently stand for methyl, ethyl, N,N-dimethylaminoethyl, propyl, n-butyl, tert-butyl, hexyl, octyl, dodecyl, 1,1-dimethyldodecyl or (1-phenyl)ethyl.

In a preferred embodiment of the process in accordance with the invention the activating additive is composed of an optionally substituted five-member aromatic N-heterocycle and at least one aluminumalkyl, whose alkyl groups can in part be replaced by halogen and/or alkoxy.

Suitable five-member aromatic N-heterocycles are ones with 1, 2, 3 or 4, preferably 1 or 2, nitrogen atoms in a five-member aromatic ring. The five-member aromatic N-heterocycles can be substituted at the ring carbon atoms by groups that are inert under the reaction conditions such as alkyl groups, preferably methyl and/or ethyl, or two adjacent carbon atoms of the five-member aromatic N-heterocycle can together belong to a fused aromatic carbocyclic system, where the aromatic carbocyclic system, in turn, can have inert groups. Examples of such N-heterocycles are the parent compounds and the substituted representatives of the pyrroles, pyrazoles, imidazoles, triazoles and tetrazoles like pyrrole, 2,5-dimethylpyrrole, indole, carbazole, pyrazole, indazole, imidazole, benzimidazole. Pyrroles and especially alkyl-substituted pyrroles, above all 2,5-dimethylpyrrole, are preferably used.

Possibilities as aluminum alkyl whose alkyl groups can in part be substituted by halogen and/or alkoxy are aluminum alkyls of the formulas AlR_3 , AlR_2Hal , AlRHal_2 , $\text{AlR}_2\text{OR}'$, $\text{AlRHalOR}'$ and $\text{Al}_2\text{R}_3\text{Hal}_3$ and their mixtures, in which R and R' independently stand for methyl, ethyl or a linear or

branched C₃-C₈ alkyl group and in which Hal stands for fluorine, bromine, iodine and above all, chlorine, for example, trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-isopropylaluminum, tributylaluminum, diethylaluminum chloride, diethylaluminum bromide, diethylaluminum ethoxide, diethylaluminum phenoxide, ethylaluminum ethoxychloride. Aluminum alkyls of the AlR₃ and AlRHal₂ type are preferably used, where triethylaluminum or a mixture of triethylaluminum and ethylaluminum dichloride are especially preferred.

/9

As alternatives to aluminum alkyls whose alkyl groups are in part replaced by halogen and/or alkoxy, it is also possible to use mixtures of the corresponding aluminum alkyls and suitable cocatalysts, from the desired mixed aluminum compounds formed in situ in the reactor.

Suitable as cocatalysts are alkyl halides, alkyl silicon halides and Lewis acid metal halides, preferably n-butyl chloride, n-butyl iodide, trimethylsilyl chloride, trimethylsilyl bromide, tin tetrachloride, germanium chloride and above all n-butyl bromide.

In the system of aluminum alkyl whose alkyl groups can in part be replaced by halogen and/or alkoxy and cocatalysts the two components are present in a mol ratio of 1:3 to 30:1, preferably 1:1 to 15:1.

In the process in accordance with the invention, the amount of the chromium compound CrX₃ or the chromium complex CrX₃L normally lies in the range from 1×10^{-7} up to 1, preferably 1×10^{-6} up to 0.1, and especially 1×10^{-5} up to 0.01, mol per kg of reaction mixture.

The amount of the five-member aromatic heterocycle normally lies in the range from 1×10^{-8} up to 100, preferably 1×10^{-7} to 1 and especially 1×10^{-5} to 0.05 mol per kg of reaction mixture.

The amount of the aluminum alkyl whose alkyl groups can in part be replaced by halogen and/or alkoxy normally lies in the range from 1×10^{-8} up to 500, preferably 1×10^{-7} to 10 and especially 5×10^{-5} to 0.5 mol per kg of reaction mixture.

In the process in accordance with the invention the mol ratio of the components (a), (b) and (c) is 1:0.1-100:0.1-500, preferably 1:0.1-10:1-100 and especially 1:1-5:5-50.

Really especially preferred is a catalyst that consists of (a) [(1,3,5-tri-n-octyl-1,3,5-triazacyclohexane)CrCl₃] or [(1,3,5-tribenzyl-1,3,5-triazacyclohexane)CrCl₃], (b) 2,5-dimethylpyrrole, and (c) triethylaluminum and ethylaluminum dichloride, where these components are in a mol ratio of 1:0.1-10:0.1-100 and preferably 1:1-5:5-50. The molar ratio of the triethylaluminum and ethylaluminum dichloride in component (c) here is 1-50:1, preferably 3-20:1.

/10

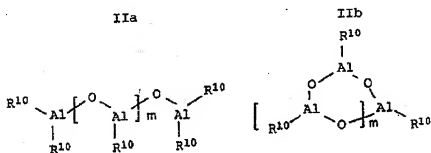
The oligomerization is preferably carried out in a solvent. As solvents for the oligomerization one can use linear, branched or alicyclic saturated hydrocarbons having 1-20 carbon atoms such as butane, pentane, 3-methylpentane, hexane, heptane, 2-methylhexane, octane, cyclohexane, methylcyclohexane, 2,2,4-trimethylpentane, decalin, linear or branched halogenated hydrocarbons like dichloroethane, aromatic hydrocarbons like benzene, toluene, xylene, ethylbenzene, mesitylene, tetralin, and the oligomer reaction products that are liquid under the reaction conditions like 1-hexene itself. These solvents can be used either individually or as mixtures.

Preferred oligomerization catalysts in accordance with the invention are in addition ones that contain an alkylaluminum as activating additive.

Here ligands L in which the groups R¹, R² and R³ independently stand in part or entirely for a group that has a substituent bonded via a carbon atom in β position or in a position still farther from the N atom of the 1,3,5-triazacyclohexane ring, especially an alkyl, aryl or silyl group, are really especially preferred. Especially preferably, this substituent is in the β position. Also especially preferred, this substituent is a β -alkyl-substituted alkyl, especially 2-ethylhexyl or 2-n-propylheptyl. Among these ligands L again really especially preferred are ones in which the groups R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ stand for hydrogen.

Suitable alkylalumoxanes are known, for example, from DE-A 30 07 725, where their structures are largely unexplained. These are products of the careful partial hydrolysis of aluminum alkyls (see DE-A 30 07 725). These products are obviously not in pure form, but rather, are in the form of mixtures of open-chain and cyclic structures of type IIa and IIb, which are presumably in dynamic equilibrium with each other.

/11



In formulas IIa and IIb the groups R^{10} are alike or different and independently stand for C_1 - C_{12} alkyl like methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, n-octyl, n-nonyl, n-decyl and n-dodecyl; C_1 - C_6 alkyl like methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n-hexyl, isohexyl, sec-hexyl are preferred, with methyl being especially preferred. m is a whole number from 0-40, preferably from 0-25, and especially preferably from 0-22.

Cage structures for alumoxanes are also discussed in the literature (see Organometallics 1996, 15, pp. 2213-26; Macromol. Symp. 1995, 97, pp. 15-25).

The alkyl alumoxanes are efficient as activating additives within the scope of this invention independent of their structural affinity.

The amount of the activating alkylaluminum compound that is used is independent of its nature. The ratio of chromium compounds CrX_3 or chromium complex CrX_3L to activating alkylaluminum compound as a rule amounts to 1:0.1 up to 1:10,000, preferably 1:1 to 1:1000.

Aprotic solvents, for example the aliphatic or aromatic hydrocarbons listed above as solvents, and especially toluene, are suitable solvents when using an oligomerization catalyst consisting of CrX_3 , a ligand L and the alkylaluminum compound or of CrX_3L and the alkylaluminum compound.

In another preferred embodiment of the process in accordance with the invention, one uses an oligomerization catalyst that contains as activating additive at least one boron compound and at least one aluminum alkyl whose alkyl group can partially be replaced by halogen and/or alkoxy. /12

Suitable boron compounds are, for example, ones with electron-attracting residues (for example, tris(pentafluorophenyl)borane, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, tri-n-butylammonium tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(perfluoromethyl)phenyl)borate, tri-n-butylammonium tetrakis(3,5-bis(perfluoromethyl)phenyl)borate and tritylium tetrakis(pentafluorophenyl)borate). These activating additives are known from EP-A 468 537 and EP-A 426 638. Tritylium tetrakis(pentafluorophenyl) borate, tris(pentafluorophenyl)borane and above all dimethylanilinium tetrakis(pentafluorophenyl)borate are preferred.

The amount of the activating boron compound that is used is dependent on its nature. The ratio of chromium compound CrX_3 or chromium complex CrX_3L to activating boron compound as a rule amounts to 1:0.1 to 1:10,000, preferably 1:1 to 1:1000.

Suitable as aluminum alkyl whose alkyl groups can partly be replaced by halogen and/or alkoxy are the representatives of this class of substances noted above, in the amounts indicated there with respect to the chromium compound CrX_3 or the chromium complex CrX_3L .

Suitable solvents in this case are aprotic solvents, for example the aliphatic or aromatic hydrocarbons listed above as solvents, and above all toluene.

Preferred olefins for the oligomerization by the process in accordance with the invention are linear and branched α -olefins having preferably 2-10, especially 2-6 and above all 2-4 carbon atoms, and their mixtures and really especially preferably, each on its own: 1-propene, 1-butene, 1-hexene, 1-decene and above all ethene, 1-butene, especially 1-butene in a mixture with its isomers, as occurs, for example, in raffinate II.

As a rule the oligomerization is to be carried out under exclusion of moisture that is as complete as possible in particular because of the tendency, above all, of the aluminum compounds and possibly the cocatalysts to hydrolyze. In doing so substantially known techniques can be used. Preferably, the process is carried out with heated equipment and under a protective gas. All of the gases that are chemically inert under the reaction conditions, expediently nitrogen or argon, can be used as protective gases. In addition, the α -olefin that is to be converted itself can take on the function of the protective gas, provided it has sufficiently high vapor pressure under the reaction conditions.

/13

The oligomerization is preferably carried out at a temperature in the range of 1-120 and especially 70-110°C and preferably at a pressure in the range of 3-120 bar. The pressure is expediently chosen so that the input mixture is in liquid form at the set temperature.

The process in accordance with the invention can be carried out batchwise or continuously, where on an industrial scale preference is to be given to the continuous mode of operation.

Reactors that are suitable for the process in accordance with the invention and for continuous conduct of the reaction are well known to one skilled in the art, for example from Ullmann's Encyclopedia of Industrial Chemistry, Volume 1, 3rd edition, 1951, pp. 743 ff.; pressure-tight reactors are described there on page 769 ff.

The other boundary conditions of such oligomerization reactions are established by one skilled in the art by means of his general knowledge in the field, which he can learn, for example, from DE-A 196 07 888.

In principle, a number of substances can be used for deactivation of the catalyst at the end of the reaction; they have in common that they are capable of hydrolyzing aluminum alkyl compounds; for example water and monoalcohols with 1-10 carbon atoms, where mineral acids can be added to these substances.

The products of the oligomerization in accordance with the invention are expediently purified by distillation. In this way, it is possible to isolate from the discharge of the ethylene oligomerization a decene and a tetradecene fraction in addition to the main (hexene) fraction that chiefly consists of 1-hexene. The decene and tetradecene fractions both consist principally of branched internal olefins.

To achieve a high overall conversion in the process in accordance with the invention unreacted starting material can be recovered and returned to the reaction.

Preferred products of the process in accordance with the invention are trimers of α -olefins, above all α -olefins with 2-6 carbon atoms, and especially 1-hexene obtainable from ethene.

The oligomers that can be obtained with the process in accordance with the invention are suitable to a particular extent for production of monoalcohols for plasticizers and surfactants. For this the oligomers are expediently subjected to hydroformylation, in which the mixtures of the aldehydes and alcohols whose chains have been lengthened by one carbon atom are formed and which are then hydrogenated to the desired alcohols. The conduct of the hydroformylation and hydrogenation are substantially known to one skilled in the art and for this reason do not require further explanation (see, for example, Beller et al., *Journal of Molecular Catalysis A* 104 (1995), pp. 17-85). /14

The following examples explain the invention.

Examples

A) Catalysts

2,5-Dimethylpyrrole, $\text{CrCl}_3(\text{THF})_3$, 1,3,5-tribenzyl-1,3,5-triazacyclohexane and triethylaluminum were obtained from Aldrich Chemical Company Ltd. and diatomaceous earth was obtained from Riedel de Haen AG.

Preparation of 1,3,5-triazacyclohexanes

Preparation of 1,3,5-tri-n-octyl-1,3,5-triazacyclohexane

100 g (0.774 mol) n-octylamine was added in small portions to a suspension of 20.2 g (0.673 mol) paraformaldehyde in 500 mL toluene that was cooled to 0°C. When the mixture was then heated to the boiling point the paraformaldehyde passed into solution. Then the water and toluene were distilled out. The residue was treated to remove volatile components at 1 mbar, taken up with 100 mL methanol, and filtered through a 1 cm thick layer of silica gel. The volatile fractions of the filtrate were then removed at 1 mbar, yielding 82.3 g (83% yield) of the title compound as a viscous clear liquid.

The following 1,3,5-triazacyclohexanes were correspondingly prepared:

- 1,3,5-tri-n-dodecyl-1,3,5-triazacyclohexane
- 1,3,5-tri-tert-butyl-1,3,5-triazacyclohexane
- 1,3,5-triethyl-1,3,5-triazacyclohexane
- 1,3,5-tris[(1-phenyl)ethyl]-1,3,5-triazacyclohexane
- 1,3,5-tris[(1,1-dimethyl)dodecyl]-1,3,5-triazacyclohexane
- 1,3-di-n-dodecyl-5-[2-(N,N-dimethylamino)ethyl]-1,3,5-triazacyclohexane
- 1,3,5-tris(2-ethylhexyl)-1,3,5-triazacyclohexane

Preparation of catalysts

Preparation of "chromium complex 1": [(1,3,5-tri-n-octyl-1,3,5-triazacyclohexane)CrCl₃]

662 mg (1.768 mmol) of the tetrahydrofuran complex CrCl₃(THF)₃ and 728 mg (1.855 mmol) 1,3,5-tri-n-octyl-1,3,5-triazacyclohexane (see above) were put at 25°C into a reaction flask. 100 mL diethyl ether dried over sodium was condensed into this mixture at -78°C. The resulting suspension was stirred for about 30 min at 25°C. Then it was filtered through a frit and the filter residue was washed with diethyl ether until the wash solution was no longer green. The residue was then dried at 25°C and 1 mbar, thus yielding 885 mg of the title compound (98% yield).

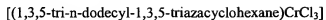
Preparation of "chromium complex 2": [(1,3,5-tribenzyl-1,3,5-triazacyclohexane)CrCl₃]

10 mL dry diethyl ether was present in a heated glass apparatus under argon at 25°C. 749 mg (20 mmol) of the tetrahydrofuran complex CrCl₃(THF)₃ was suspended therein, and a solution of 715 mg (20 mmol) 1,3,5-tribenzyl-1,3,5-triazacyclohexane in 2 mL diethyl ether was added by drops to this mixture while stirring. Then the mixture was stirred for another 30 min at 20°C and then filtered under argon through a frit. The filter residue was washed three more times, each time with 10 mL diethyl ether, and then dried at 25°C and 1 mbar. In this way 0.64 g of the title compound was obtained as a violet solid.

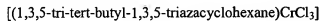
Preparation of the "chromium complexes 3-10"

The following complexes of chromium(III) chloride were prepared by analogy with the preparation of the complexes 1 and 2:

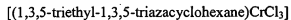
"Chromium complex 3":



"Chromium complex 4":

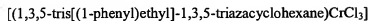


"Chromium complex 5":



"Chromium complex 6":

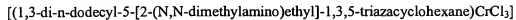
/16



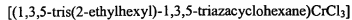
"Chromium complex 7":



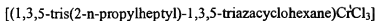
"Chromium complex 8":



"Chromium complex 9":



"Chromium complex 10":



B) Oligomerizations

Example 1: Oligomerization of ethene in the presence of "complex 1" and 2,5-dimethylpyrrole

A steel autoclave with a volume of 100 mL was heated in a stream of argon at 105°C for 60 min. Then at 25°C 14.5 mg "chromium complex 1" was added to the autoclave and then 25 mL n-heptane dried over sodium and 0.5 mL of a solution of 143 mg 2,5-dimethylpyrrole in 10 mL n-heptane, which corresponds to 0.075 mmol 2,5-dimethylpyrrole were added. The autoclave was then flushed three times with ethene at normal pressure. This was followed by the addition of 0.75 mL of a 1-molar solution of triethylaluminum in n-heptane, whereupon ethene pressure of 25 bar was connected. Then the temperature was raised to 80°C and the ethene pressure was increased to 40 bar. The contents of the autoclave were stirred for 2 h under these conditions; then the autoclave was cooled and depressurized. The catalyst was deactivated by adding 1 mL water to the reaction mixture. The components that were insoluble in the reaction mixture were separated, dried and weighed. Calculated with respect to 1 g chromium in the catalyst, the productivity was 18.6 kg. The relative amounts of the products that were obtained were determined by gas chromatography with n-heptane as internal standard:

Hexenes	44.4 wt%
Decenes	33.1 wt%
Tetradecenes	10.9 wt%
"Polymers"	1.5 wt%

Examples 2-11

/17

Examples 2-11 were carried out by analogy with Example 1. n-Butyl bromide (n-BuBr) and ethylaluminum dichloride (EADC) were used as 0.1M solutions in n-heptane. The starting substances, the pertinent amounts and the results of the experiments are summarized in the following Table 1.

/18

TABLE 1. Data for Examples 2-11

①	②	③			④	⑤	⑥	⑥	⑥	⑦	⑧
Bsp.	Chrom-Kom- plex CrX ₃ L	Kat [μmol]	DMP [μmol]	TEA [μmol]	Cokat [μmol]	n-Heptan [ml]	C6 [Gew.-%]	C10 [Gew.-%]	C14 [Gew.-%]	Polym [Gew.-%]	Produktivität [kg/g Cr]
2	2	25	75	750	-	25	56,1	27,5	6,5	7,3	27,4
3	2	10	30	300	-	10	62,1	21,7	4,7	7,6	44,8
4	3	10	30	300	-	10	53,5	25,0	6,3	9,1	33,5
5	4	10	30	300	-	10	59,4	24,4	7,3	2,6	21,1
6	5	10	30	300	-	10	63,3	21,1	5,3	8,8	16,4
7	6	10	30	300	-	10	55,6	23,9	7,0	4,4	19,3
8	7	10	30	300	-	10	61,7	23,5	6,0	4,9	28,0
9	8	10	30	300	-	10	48,3	23,0	7,0	10,5	24,8
10	2	10	30	300	n-BuBr 30	10	68,1	20,7	6,2	2,2	75,3
11	2	10	30	300	EADC 30	10	82,8	14,3	2,1	0,3	106,1

Abbreviations:

Cat Amount of chromium complex

CrX₃L

DMP Amount of 2,5-dimethylpyrrole

TEA Amount of triethylaluminum

Cocat Cocatalyst and amount

n-Heptane Amount of n-heptane

C6 Amount of hexenes in product

C10 Amount of decenes in product

C14 Amount of tetradecenes in product

Polymer Polymer fractions in product

Key: 1 Example

2 Chromium complex

CrX₃L

3	Cat [μmol]
4	Cocat [μmol]
5	n-Heptane [mL]
6	[wt%]
7	Polymer
8	Productivity

Example 12: Trimerization of 1-butene in the presence of "chromium complex 9" and methyl aluminoxane, and hydroformylation of the resulting trimer to the corresponding oxoalcohol

/19

a) Trimerization

A steel autoclave with a volume of 2500 mL was heated in a stream of argon at 120°C. At 25°C 750 mg "chromium complex 9" and 500 g toluene dried over sodium were put into the autoclave, and then the autoclave was flushed three times with 1-butene. Then 50 g of a 1M solution of methyl alumoxane in toluene was added and 500 g 1-butene was added to the autoclave via a lock. Then the temperature in the autoclave was raised to 40°C and the pressure adjusted to 15 bar with nitrogen gas. After 2 h of reaction under these conditions the autoclave was cooled and depressurized. The catalyst was deactivated by adding 2-propanol. In the subsequent gas chromatographic analysis only dodecene isomers were found as oligomers in the reactor discharge (800 g). The dodecene mixture obtained by hydrogenation had an ISO index of 2.3.

b1) Hydroformylation in the presence of cobalt carbonyl

1.06 kg of the dodecene mixture produced in section (a) was hydroformylated with 4.0 g $\text{CO}_2(\text{CO})_8$ at 185°C and 280 bar CO/H_2 (1:1) with the addition of 100 g water, in a 2500 mL rotary stirred autoclave and agitated for 5 h. The cobalt was then removed from the reaction discharge by oxidation with 10% acetic acid while admitting air at 90°C. The resulting oxo product was hydrogenated in a 2500 mL stirred reactor in trickle mode on a Co/Mo fixed bed catalyst at 175°C and 280 bar H_2 with the addition of 10% water with respect to the organic phase. The resulting alcohol mixture was processed by distillation and the tridecanol mixture isolated in this way had an OH number of 279 mg KOH/g. An average degree of branching of 2.7 was determined by ^1H NMR spectroscopic analysis.

b2) Hydroformylation with rhodium biscarbonylacetylacetonate/polyethyleneimine

50 g rhodium biscarbonylacetylacetonate, 4.5 g of a polyethyleneimine with molecular weight $M_w = 460,000$, in which 60% of all nitrogen atoms were amidated with lauric acid, 800 g of the dodecene mixture produced in section (a) and 196 g toluene were heated in a 2500 mL stirred lift autoclave under CO/H_2 (1:1) to 150°C. A pressure of 280 bar was established by means of CO/H_2 . After 7 h the autoclave was cooled, depressurized and emptied. Olefin conversion of 93% was determined by gas chromatography. The resulting oxo product was hydrogenated in a 2500 mL tubular reactor in trickle mode on a Co/Mo fixed bed catalyst at 175°C and 280 bar H_2 with the addition of 10 wt% water with respect to the organic phase. The resulting alcohol mixture was processed by distillation and the resulting tridecanol mixture had an OH number of 279 mg KOH/g. An average degree of branching of 2.9 was determined by ^1H NMR spectroscopy. /20

Examples 13-22: Trimerization in the presence of "chromium complex 9" and methylaluminoxane

a) Alternative production of "chromium complex 9"

15 mL (+/-)-2-ethylhexylamine (92 mmol) was dissolved in 200 mL toluene, and 2.75 g paraformaldehyde (92 mmol) was added. After stirring the mixture for 1 h the toluene/water azeotrope was distilled out until a boiling point of 110°C was reached. Then it was cooled in a stream of argon to below the boiling point and 4.82 g water-free CrCl_3 (31 mmol) was added. After renewed distillation of a few mL toluene and cooling in a stream of argon 0.5 g zinc powder was added. With further distillation of the toluene a deep violet solution was obtained from the suspension. Toluene was distilled out for another 30 min and the residue was cooled to 25°C. After the zinc powder had settled the deep violet solution was decanted out in air and the solvent removed in a rotary evaporator. The violet, somewhat oily solid residue was dissolved in acetone and filtered. The resulting deep violet solution was mixed with water until the solutions standing over the violet precipitate was only a weakly violet color. After filtration the violet residue was in the end dried at 50°C in a vacuum (about 1 Pa) for 40 h. 13.12 g (74%) of the violet "chromium complex 9" was obtained.

b) Conducting trimerizations

The trimerizations were carried out in a 1-L four-neck flask provided with a contact thermometer, stirrer, heating mantle and gas inlet tube, in which between 30 and 50 μmol "chromium complex 9" in 250 mL toluene was present under argon at 40°C.

Methylalumoxane ("MAO") was used in the form of a 1.6M solution in toluene.

Dimethylanilinium tetrakis(pentafluorophenyl) borate ("DMAB") served as the boron compound.

After adding it the reaction mixture was heated to 70°C, then cooled to 40°C and then mixed with triisobutylaluminum ("TIBAL").

/21

20-40 L/h ethene or 1-butene was passed through the pale green/yellow solution obtained after the addition of the MAO or the DMAB/TIBAL or a corresponding amount of 1-hexene was added by drops.

During the experiment on the reaction time t , the temperature was kept constant at temperature T . The reaction was stopped by adding 15 mL concentrated hydrochloric acid in 50 mL methanol and the reaction mixture was then stirred for another 15 min. Then 250 mL methanol was added and the mixture was stirred for another 15 min. After filtering out any insoluble polymer that might have formed the product was washed three times with water and dried over sodium sulfate. The yield and product distribution were determined by gas chromatography from the solution obtained in this way. Other data on starting material and the results of the experiments can be found in Table 2.

/22

TABLE 2. Data for Examples 13-22

1 Exp.	2 Menge Chrom-Komplex 9		3 Atomver- hältnis Al:Cr	4 Atomver- hältnis B ¹ :Cr	T [°C]	Monomer	5 DMP ¹ [μmol]	t [min]
	[mg]	(μmol)						
13	16,6	33,6	300:1	-	40	C ₂ H ₄ +5 ml 1-Hexen	5	60
14	19,0	32,6	350:1	-	40	C ₂ H ₄ ^a	-	60
15	30,2	51,9	50:	2,2:1	40	C ₂ H ₄ ^a	-	60
16	25,5	43,8	350:1	-	40	C ₂ H ₄ ^a	-	60
17	23,8	40,9	50:1 ^b	2:1	40	500 ml 1-Hexen	123	90
18	20,4	35,1	50:1	2:1	40	500 ml 1-Hexen	5	-
19	21,2	36,4	300:1	-	40	500 ml 1-Hexen	-	60
20	26,6	45,7	350:1	-	40	1-Buten ^a	-	60
21	22,2	38,1	50:1	10:1	40	1-Buten ^a	6	60
22	18,4	31,6	300:1	-	20	1-Buten ^a	-	60

TABLE 2. Data for Examples 13-22 (cont.)

Bsp. (1)	Polymer (g)	(7) Produkte (g)				(8) Aktivität des verwendeten Katalysators (kg/(mol Cr·h))					(9) Gesamt
		C ₆	C ₁₀	C ₁₄	C ₁₈	Polymer	C ₆	C ₁₀	C ₁₄	C ₁₈	
13	-	13,0	16,5	3,08	-	-	387	488	91	-	965
14	0,52	6,9	10	2,3	-	16	213	307	71	-	607
15	0,9	4,9	7,78	2,5	-	17	94	149	48	-	308
16	0,56	5,96	12,5	2,99	-	12,8	136	286	68	-	502
17	-	-	-	-	3,47	-	-	-	-	84	84
18	-	-	-	-	1,02	-	-	-	-	29,1	29,1
19	-	-	-	-	2,7	-	-	-	-	75,8	75,8
20	-	-	2,08	-	-	-	-	-	43,1	-	43,1
21	-	-	2,58	-	-	-	-	-	67	-	67
22	-	-	1,19	-	-	-	-	-	37,65	-	37,65

¹ Activation takes place by adding DMAB and TIBAL

² Triethylaluminum was used instead of TIBAL

³ 2,5-Dimethylpyrrole

⁴ Gas was passed through the mixture

- Key:
- 1 Example
 - 2 Amount of chromium complex 9
 - 3 Al:Cr atomic ratio
 - 4 B¹⁾:Cr atomic ratio
 - 5 1-Hexene
 - 6 1-Butene
 - 7 Products [g]
 - 8 Activity of catalyst [kg/(mol Cr*h)]
 - 9 Total

Examples 23-26: Trimerization in the presence of "chromium complex 10" and methylalumoxane

/24

a) Alternative production of "chromium complex 10"

The preparation took place by analogy with the alternative preparation of chromium complex 9 in accordance with Examples 13-22.

b) Conducting trimerizations

The trimerizations of Examples 23-25 were carried out by analogy with Examples 13-22 in toluene as solvent.

The reaction in accordance with Example 26, on the other hand, took place in a 1000 mL autoclave at a pressure of 40 bar, likewise in toluene.

The other data on starting materials and the results of the experiments can be found in Table 3.

/25

TABLE 3. Data for Examples 23-26

1 Bsp.	2 Menge Chron-Komplex 10		3 Atonverhältnis Al:Cr	4 Atonverhältnis B ¹⁾ :Cr	T [°C]	Monomer	DMP ³⁾ [μmol]	t [min]
	[mg]	[μmol]						
23	19,5	29,3	300 : 1	-	40	C ₂ H ₄ ⁴⁾	-	60
24	28,3	42,5	50 : 1 ⁵⁾	5,3 : 1	40	1-Buten ⁴⁾	127,5	60
25	12,1	18,2	500 : 1	-	50	6) Ethen	-	30
26	55	83	300 : 1	-	40	200 ml 1-Buten ⁵⁾	-	60

1 Bsp.	Polymer	7 Produkte [g]					8 Aktivität des verwendeten Katalysators [kg/[mol Cr·h]]					9
	[g]	C ₆	C ₁₀	C ₁₄	C ₁₈		Polymer	C ₆	C ₁₀	C ₁₄	C ₁₈	Gesamt
23	0,43	9,02	10,9	2,06	0,16		14,7	308	372	70	5,5	770
24	-		C ₁₂ : 2,31				-		C ₁₂ : 54,3			54,3
25	0,07	6,63	1,96	-	-		3,8	730	215	0	0	945
26	-		C ₁₀ : 0,24, C ₁₂ : 2,09				-		C ₁₀ : 2,9, C ₁₂ : 25,2			28,1

¹ Activation takes place by the addition of DMAB and TIBAL

² Triethylaluminum was used instead of TIBAL

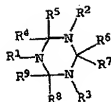
- ³ 2,5-Dimethylpyrrole
- ⁴ Gas was passed through the mixture
- ⁵ Use of triethylaluminum

Key:	1	Example
	2	Amount of chromium complex 10
	3	Al:Cr atomic ratio
	4	B ^D :Cr atomic ratio
	5	1-Butene
	6	Ethene
	7	Product [g]
	8	Activity of catalyst [kg/(mol Cr*h)]
	9	Total

Claims

/26

1. An oligomerization catalyst for olefins obtained from
 - a) a chromium compound CrX_3 and an at least equimolar amount, with respect to the chromium compound CrX_3 , of a ligand L, or a ready-to-use chromium complex CrX_3L , in which the groups X independently stand for extractable counterions and L stands for a 1,3,5-triazacyclohexane of formula I



I

in which the groups R^1 - R^9 independently have the following meanings: hydrogen or Si-organic or optionally substituted C-organic groups with 1-30 C atoms, where two geminal or vicinal residues R^1 - R^9 can also be bonded to a five- or six-member ring, and

b) at least one activating additive.

2. An oligomerization catalyst as in Claim 1, obtainable by using an activating additive from an optionally substituted five-member aromatic N-heterocycle and at least one aluminum alkyl, the alkyl groups of which can in part be replaced by halogen and/or alkoxy.

3. An oligomerization catalyst as in Claim 1, obtainable by using at least one activating additive.

4. An oligomerization catalyst as in Claim 1, obtainable by using at least one boron compound and at least one aluminum alkyl, the alkyl groups of which can in part be replaced by halogen and/or alkoxy, as activating additive.

5. An oligomerization catalyst as in Claims 1-4, characterized by the fact that in the 1,3,5-triazacyclohexane I the groups R^1 , R^2 and R^3 independently stand for optionally substituted C_1 - C_{12} alkyl, C_6 - C_{15} aryl or C_6 - C_8 arylalkyl.

/27

6. An oligomerization catalyst as in Claim 5, characterized by the fact that in the 1,3,5-triazacyclohexane I the groups R^1 , R^2 and R^3 independently stand for optionally substituted C_1 - C_{12} alkyl or C_6 - C_8 arylalkyl.

7. An oligomerization catalyst as in Claims 1-6, characterized by the fact that in the 1,3,5-triazacyclohexane I the groups R^4 , R^5 , R^6 , R^7 , R^8 and R^9 independently stand for hydrogen or methyl.

8. A method for producing oligomers with up to 30 carbon atoms by the reaction of an olefin or a mixture of olefins at temperatures from 0-150°C and pressures from 1-200 bar in the presence of an oligomerization catalyst as in one of Claims 1-7.

9. Oligomers obtainable by the method given in Claim 8.

10. Oxo alcohols obtainable by substantially known hydroformylation of the oligomers as in Claim 9.

11. [(1,3,5-Tris(2-n-propylheptyl)-1,3,5-triazacyclohexane)CrCl₃].

12. [(1,3,5-A₃-1,3,5-triazacyclohexane)CrCl₃], in which A stands for an alkyl that is alkyl substituted in position 2.

Int. Patent Application No.
PCT/EP 00/02660

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07F11/00 C07C29/16 C07C2/32 B01J31/18

According to [International] Patent Classification (IPC) or to both national classification and IPO

B. FIELDS SEARCHED

IPC 7 C08F C07F C10G C07C B01J

Documentation searched other than original documentation to the extent that such documents are included in the fields searched.

†Literature data have been consulted during the international search phase of data base and, where practical, search terms used.

CHEM ABS Data, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Choice of document, with indication, where appropriate, of the relevant paragraph
-----------	---

Patented by claim No.

A CHEMICAL ABSTRACTS, vol. 129, no. 18,
2 November 1998 (1998-11-02)
Columbus, Ohio, US:
abstract no. 231170.
TANI, KAZUHIDE ET AL: "Preparation
of alpha.-olefin polymers by the use of
vanadium or chromium complex catalysts"
XP002139748
abstract
& JP 10 231317 A (MITSUBISHI CHEMICAL
INDUSTRIES LTD., JAPAN)
2 September 1998 (1998-09-02)

1-12

A EP 0 537 609 A (ETHYL CORP)
21 April 1993 (1993-04-21)
cited in the application
examples 1-15; table 1

1-12

-/-

Y Further documents are listed in the continuation of box G.

Y Patient family members are listed in annex.

* Search / extension of cited documents :

A documents defining the general state of the art which is not considered to be of particular relevance

* If not a document but published on or after the international
file date

* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

* document referring to an oral disclosure, use, exhibition or other means

* documents published prior to the International filing date but later than the priority date claimed

The abstracts published after the International Day date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention.

* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken into account

* documents of particular relevance the defined investigation cannot be considered to involve an excessive step in the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* designated member of the same patent family

Date of the actual completion of the international search

On the way of making of the International search report.

4 September 2000

11/09/2000

Name and mailing address of the ISA
European Patent Office, P.O. 5010 Ravensden 2
M. - 2250 HV Rijswijk
Tel. (+31-70) 340-2222, Tx. 31 031 apo st.
Fax (+31-70) 340-0015

Authorized officer _____

Part IV. J

From ECJ 254/8322 forwarded about 1 July 1982

page 1 of 2

INTERNATIONAL SEARCH REPORT

No. Serial Application No.
PCT/EP 00/02660

D. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Character of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 00 34211 A (BP CHEMICALS LIMITED, UK) 15 June 2000 (2000-06-15) page 3, line 1 - page 7, line 6: claim 1	1-12

Form PCT/ISA/210 (second sheet) (July 1992)

page 2 of 2

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Appl. No.

PCT/EP 00/02660

Patent documents cited to search report	Publication date	Patent family member(s)	Publication date
JP 10231317 A	02-09-1998	NONE	
EP 0537609 A	21-04-1993	CA 2079399 A	17-04-1993
		DE 69212761 D	19-09-1996
		DE 69212761 T	02-01-1997
		JP 5221882 A	31-08-1993
		US 5968866 A	19-10-1999
		US 5550305 A	27-08-1996
		US 5811618 A	22-09-1998
		US 5744677 A	28-04-1998
NO 0034211 11 A		NONE	

Form PCT/ISA/290 (patent family search) (July 2002)